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"Threshold Phenomena in Nonlinear Currents upon Metallization of Si(001)

by

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Metal-semiconductor interfaces form rectifying Schottky junctions of crucial technological significance.[1] On a more fundamental level, the metallization of a semiconducting surface provides an opportunity to study a novel insulator-metal transition in a two-dimensional system.[2] Despite numerous studies in this area, the relationship between the physics of the insulator-metal transition and the technology of Fermi level pinning and Schottky barrier formation has not been firmly established for many systems.[3,4]

The intensively studied model systems of alkali metals adsorbed onto Si(001) are prime examples where this relationship continues to be elusive. For potassium adsorption, early experiments observing the reversal of the work function change beyond a minimum value at a relatively high coverage ($\theta \sim 0.5$-0.6 monolayers) were interpreted to demonstrate that the surface is metallic only at coverages higher than this.[5,6] Electron scattering experiments assigned the insulator-metal transition to occur at lower coverage at the threshold for observing a feature thought to be a collective plasma excitation.[7] A recent angle-resolved photoemission and inverse photoemission study concluded that the surface becomes metallic at the work function minimum,[8] while a contemporaneous core level photoemission measurement[9] deduced a much lower transition coverage, $\theta \sim 0.25$. The potassium coverage at which the Fermi level becomes pinned is currently in dispute.[6,8]

None of these experiments have attempted to measure directly the most distinguishing feature of a metal: non-activated transport of charge. We have applied second harmonic generation (SHG)[10] in an attempt to accomplish this. By choosing a particular combination of fundamental and harmonic polarizations and monitoring the change in both the phase and the intensity of the SH light, we are able to probe selectively the non-linear currents induced parallel to the surface plane. These currents are sensitive to the surface dielectric function and thus to the

in-plane surface conductivity. For all three alkalis we observe an abrupt increase in SH intensity and change in relative SH phase at a coverage of very nearly one sixth of a monolayer (ML). We investigate various sources which might cause such thresholds, and speculate that they correspond to an insulator-metal transition. The transition coincides with a recently-observed low-coverage (2x3) structure for K and Cs/Si(001), implying that these structures are Mott-Hubbard-like insulators.

The sample used was cut from a commercial n-type Si(100) wafer and was cleaned in ultrahigh vacuum by cycles of neon ion bombardment and heating to 1200K. After annealing at 1150K for 1 min. and slow subsequent cooling, a two domain 2x1 reconstruction was observed. The sample was then positioned 4 cm. from a carefully degassed alkali chromate dispenser (SAES) for deposition and corresponding SHG and work function measurements. The coverage was calibrated with work function and Auger electron spectroscopy, assuming that the work function minimum occurs at Θ = 0.55 and 0.63 ML, for Cs[11] and K[12], respectively, and that the work function achieves its asymptotic value for Na adsorption at Θ = 0.7 ML.[13] The work function was measured by threshold photoemission using a Xe arc lamp and a monochromator to select the photon energy. The SHG experiments were performed using the 1.064 μm output of a 10 Hz Nd:YAG laser of 10ns pulse duration focused into a spot 3 mm in diameter. The SH intensity following a <3mJ/pulse excitation was measured in real time during alkali deposition. The SH phase relative to a fixed reference was measured by an interference technique similar to that described previously.[14]

The significance of measuring currents parallel to the surface plane is demonstrated by the results in Fig. 1. Panel a presents an expanded view of the s-polarized SH intensity for mixed (sp) input polarization [$I_{ms}(2\omega)$] as a function of alkali coverage. As discussed further below, this combination of polarizations probes specifically the parallel nonlinear currents. A distinct threshold response is

observed at Θ = 0.17±0.02 ML for all three alkalis. Below this coverage the SH intensity is small and constant to within our noise level. Even more dramatic thresholds are observed in Fig. 1b, which presents the corresponding relative phase change of the light as a function of alkali coverage. By contrast, other more commonly employed SHG polarization schemes, which probe the nonlinear currents perpendicular to the surface, exhibit only weak changes in slope at the threshold coverage.[15] The work function is also most sensitive to the dipolar response normal to the surface. As shown in Fig. 1c, this exhibits a relatively smooth decrease at low coverage, followed by a reversal for potassium and cesium, but not for sodium.[11-13] The abrupt thresholds at a common low coverage in Fig. 1a and 1b might be associated with gradual changes in slope in the coverage dependence of the work function, but are clearly not simply related to the work function minima which occur at different higher coverages for the three alkalis.

Further desposition yields an overall enhancement of the SH intensity by typically two orders of magnitude (Fig. 1d) and a maximum phase advance of roughly 0.5 π, π, and 1.3 π for Na, K, and Cs, respectively. The maximum SH signal and the maximum of the SH phase advance occur precisely at the coverage where the work function minimizes for K and Cs. For Na, no reversal in the work function change is observed, and, correspondingly, the SH data do not exhibit well-defined extrema. The precise correlation between work function minima and SH extrema indicates that the SH energy is approached by an optical resonance at an energy given by the work function. This association has been suggested in the past,[16] although it is not always observed (even in these systems) due either to domination by interband transitions or to the presence of interference effects when other polarization schemes are used.[15] At lower coverage distinct shoulders in SH intensity are observed in Fig. 1d for K and Cs, and perhaps also Na. These shoulders shift systematically to lower coverage for heavier alkali. Further analysis

suggests that these correspond to the coverage at which the fundamental photons are resonant with the collective plasma excitations of the film.[15] This already implies that the surface is metallic at coverages below these shoulders.[7]

Our SHG results thus exhibit three significant features: a low coverage threshold, a plasmon resonance, and a work function resonance. We will discuss the origin of and relationship between these features for the balance of this letter.

We first discuss how this combination of polarizations allows us to probe specifically the parallel nonlinear currents. SHG, in the electric dipole approximation, is forbidden in the bulk of centrosymmetric crystals.[10] At an interface, the spatial inversion symmetry is lost and a surface second order polarization can be induced by intense electromagnetic radiation.[10] In addition, the field discontinuity at the interface contributes a strong quadrupolar second order polarization. The generalized SH polarization $\mathbf{P}(2\omega)$, where the SH current $\mathbf{J}(2\omega) = \partial\mathbf{P}(2\omega)/\partial t$, is related to the fundamental excitation field $\mathbf{E}(\omega)$ by

$$\mathbf{P}(2\omega) = \chi^{(2)} : \mathbf{E}(\omega)\,\mathbf{E}(\omega) \qquad (1).$$

The non-zero elements of the susceptibility tensor $\chi^{(2)}$ for a (100) surface with 4mm symmetry are $\chi_{\perp\perp\perp}$, $\chi_{\perp\parallel\parallel}$, $\chi_{\parallel\perp\parallel}$, where $\parallel$ is a direction in the surface plane, and $\perp$ is the direction normal to it. These elements, in the presence of a two-domain (2x1) reconstruction on Si(001), lead to an azimuthally isotropic SH response.[15] The susceptibility tensor in Eq. 1 is complex. Thus, the nonlinear currents and the SH fields are characterized by their amplitude as well as their phase relative to a fixed reference. The results in Figs. 1 indicate that measuring both the intensity and relative phase of the SH light is essential to provide a good measure of the dielectric properties of this surface.

That the data in Fig. 1 provide a measure of the nonlinear currents parallel to the surface plane can be seen by using an approach parallel to the hydrodynamical model of Rudnick and Stern.[17] The vector velocity and scalar charge density are modelled as harmonic series. The parallel nonlinear current density is then given by:

$$J_{\parallel}(2\omega) = n_o v_{\parallel}(2\omega) + n(\omega) v_{\parallel}(\omega) \qquad (2)$$

where n_o is the static electronic charge density, $n(\omega)$ is the first order bound charge density oscillation given in Maxwell's equations as $\mathrm{div}[E(\omega)]/4\pi$, and $v_{\parallel}(\omega)$ and $v_{\parallel}(2\omega)$ are the fundamental and SH charge velocity oscillations parallel to the surface plane. The dominance of the second term in Eq. 2 is ensured by the large gradient of the normal field component near the surface, i.e., the important source term in our experiment is quadrupolar in nature.[15] Since this term contains only linear parameters, the nonlinear SHG results in Fig. 1 can be understood entirely in terms of the linear dielectric properties in the surface region. Simply stated, the p-polarized component of the fundamental $[E_{\perp}(\omega)]$ induces a modulation in the charge density, while the s-polarized component $[E_{\parallel}(\omega)]$ induces a velocity modulation parallel to the surface plane. The product of these leads to a parallel generalized SH polarization $P_{\parallel}(2\omega)$ through a single tensor element, $\chi_{\parallel\perp\parallel}$, in Eq. 1. The associated current $J_{\parallel}(2\omega)$ then radiates an s-polarized SH field. Thus, for the geometry in Fig. 1, the SH signal is enhanced by large induced charge oscillations normal to the surface and by large velocity oscillations parallel to the surface.

The simplicity of this analysis provides hope that the SH results in Fig. 1 might be understood in terms of simple, phenomenological models. The source of the two resonances is apparent in Eq. 2. The restoring force for the induced charge

density oscillation $n(\omega)$ is related to the work function, and a resonance at this energy naturally follows. Also, the frequency-dependent linear conductivity will be associated with a linear dielectric response function having a plasma resonance at an energy related in monotonically increasing fashion to the free carrier density. As the free carrier density increases upon metallization, the plasma energy will traverse a resonance with the fundamental photon energy. Our results suggest that, above threshold, the free carrier density increases more quickly for the heavier alkali, in line with expectations based upon the reducing electronegativity. The source of the threshold behaviors in Fig. 1 is less obvious. It is unlikely that these are associated with either of the above resonance phenomena, since the coverages of the latter are strongly alkali-dependent while those of the thresholds are not. The measured phase advances also exclude the possibility of there being additional resonances. Traversing a resonance with either the fundamental or SH frequency yields a π phase shift. The phase measurements (Fig. 1b) are consistent with the plasma resonance crossing ω and the work function resonance approaching (but not crossing) 2ω as the coverage is increased. No other resonances can contribute, and the value of the plasma energy at saturation thus lies between the fundamental and SH energies. Moreover, we have tried unsuccessfully to fit the thresholds with resonance profiles. We therefore conclude that the observed thresholds arise from a separate mechanism not related to any resonance phenomenon.

We speculate that the thresholds observed in Fig. 1b and 1c result from the absence of free charge carriers below $\theta \sim 0.17$, i.e., to the occurrence of an insulator-metal transition at this coverage. This coverage is comparable to those reported in recent electron scattering[7] and core level photoemission experiments for K/Si(001),[9] although the transition is more distinct in the present measurement. It is intuitively satisfying to relate the thresholds to such a transition, since larger parallel currents would be induced in a metal than in an insulator, leading to

enhanced SH intensity. It is surprising and significant that the three alkalis all exhibit the transition at essentially the same fractional coverage.[18] For free-standing monolayer films, the size of the alkali s-orbital would certainly impact the density at which a Mott transition would occur. We therefore conclude that the insulator-metal transition is not a simple Mott-Hubbard transition driven by changes in adsorbate density.[19] The common thresholds suggest that a relevant geometric structure determined by the Si(001) (2x1) surface is shared by all three alkalis near $\Theta \sim 0.17$ ML. For both Cs and K/Si(001), at one-sixth ML an ordered (2x3) structure has been observed;[20,21] a similar structure has been suggested for Na/Si(001).[22] A possible representation of this structure, based upon recent STM measurements,[23] is given in Fig. 2. In a one-electron scheme, this structure would necessarily be metallic. We propose that the (3x2) phase is a Mott-Hubbard or charge-transfer insulator, probably exhibiting antiferromagnetic ordering at low temperature. Further deposition of alkali atoms is analogous to the addition of small amounts of donor impurities which initially would fill the upper Hubbard or charge-transfer band and hence would exhibit metallic behavior.[19] As the system becomes more metallic with increasing alkali coverage, the on-site correlation energy is progressively screened and the free-carrier density and SH response increases rapidly.

A similar correlated-insulator ground state has been suggested for Cs on GaAs(110).[2] In that case, however, the surface remains insulating up to completion of the first monolayer. It is surprising that the metallic phase occurs at such a relatively low coverage for alkalis on Si(001). This difference is suggestive of more substantial through-surface interaction of the correlated electrons in the (2x3) phase in these systems than for Cs/GaAs(011).

We now briefly outline the simplest model which might test the above reasoning; more details will be given in a future publication.[15] The interfacial

metallic region is modeled as an isotropic film of jellium bounded by a semifinite Si dielectric substrate on one side and by vacuum on the other. This gross simplification of these complex systems is not expected to fit our results precisely, but should, for example, encompass the observed threshold and predict the correct order of magnitude SH intensity increase (Fig. 1d) and the overall SH phase change (Fig. 1b). Parallel to the film, the electrons are allowed to respond freely in a hydrodynamical fashion, and a Drude dielectric function with plasma frequency ω_p and scattering time τ is assumed. The localization of the carriers perpendicular to the surface is modeled using an oscillator dielectric function characterized by a natural frequency ω_o equal to the work function and damping frequency Γ.

This model provides a satisfactory treatment of our SH intensity results. The most important free parameter is ω_p, which depends parametrically upon the metallic carrier density. The thresholds can only be simulated by an onset in ω_p, and thus in the metallic screening charge, near one-sixth of a monolayer. Unfortunately, while the same parameters provide a good fit to the magnitude of the phase, its sign is predicted to be in the opposite direction from that observed in Fig. 1b. Clearly a more detailed microscopic theory is needed to provide a complete understanding of our results.

In summary, we have demonstrated a method for monitoring surface conductivity via excitation of parallel surface currents by surface SHG. We have used this technique to observe unusual thresholds in SH intensity and relative phase at a coverage corresponding approximately to that at which the Fermi level is pinned.[6] The most natural interpretation for these thresholds is that they correspond to a transition from a correlated insulator to a metallic ground state.

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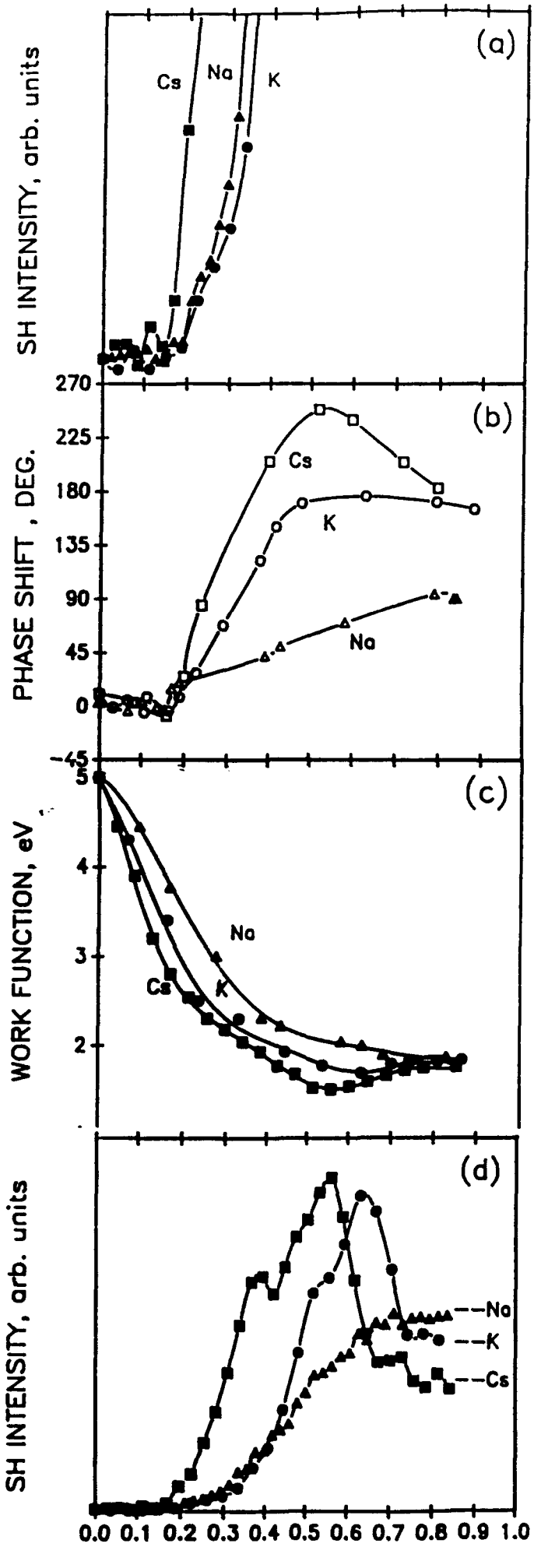
FIGURE CAPTIONS

Fig. 1: a) Expanded plot of SH intensity [$I_{ms}(2\omega)$] vs. alkali coverage for mixed (sp) input polarization and s-polarized SH light. b) SH relative phase vs. alkali coverage for the same polarizations as in b). c) Work function change, $\Delta\Phi$, vs. alkali coverage, Θ, on Si(100)2x1. The bare surface work function is extrapolated to 5.0 eV. d) SH intensity as a function of alkali coverage scaled to show the resonance features at higher coverage. Solid curves are intended to guide the eye.

Fig. 2: Proposed structure for a single domain of the Si(001)-(2x3)K overlayer at 1/6 ML having a correlated insulator ground state. Large filled circles are the potassium atoms, while the open and shaded smaller circles are the lower and upper silicon surface dimer atoms, respectively.

Fig. 1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Cs
Na
K
SH INTENSITY, arb. units
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PHASE SHIFT , DEG.
Cs
K
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2
WORK FUNCTION, eV
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K
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SH INTENSITY, arb. units
--Na
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0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
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Si (001) - 2x3 K

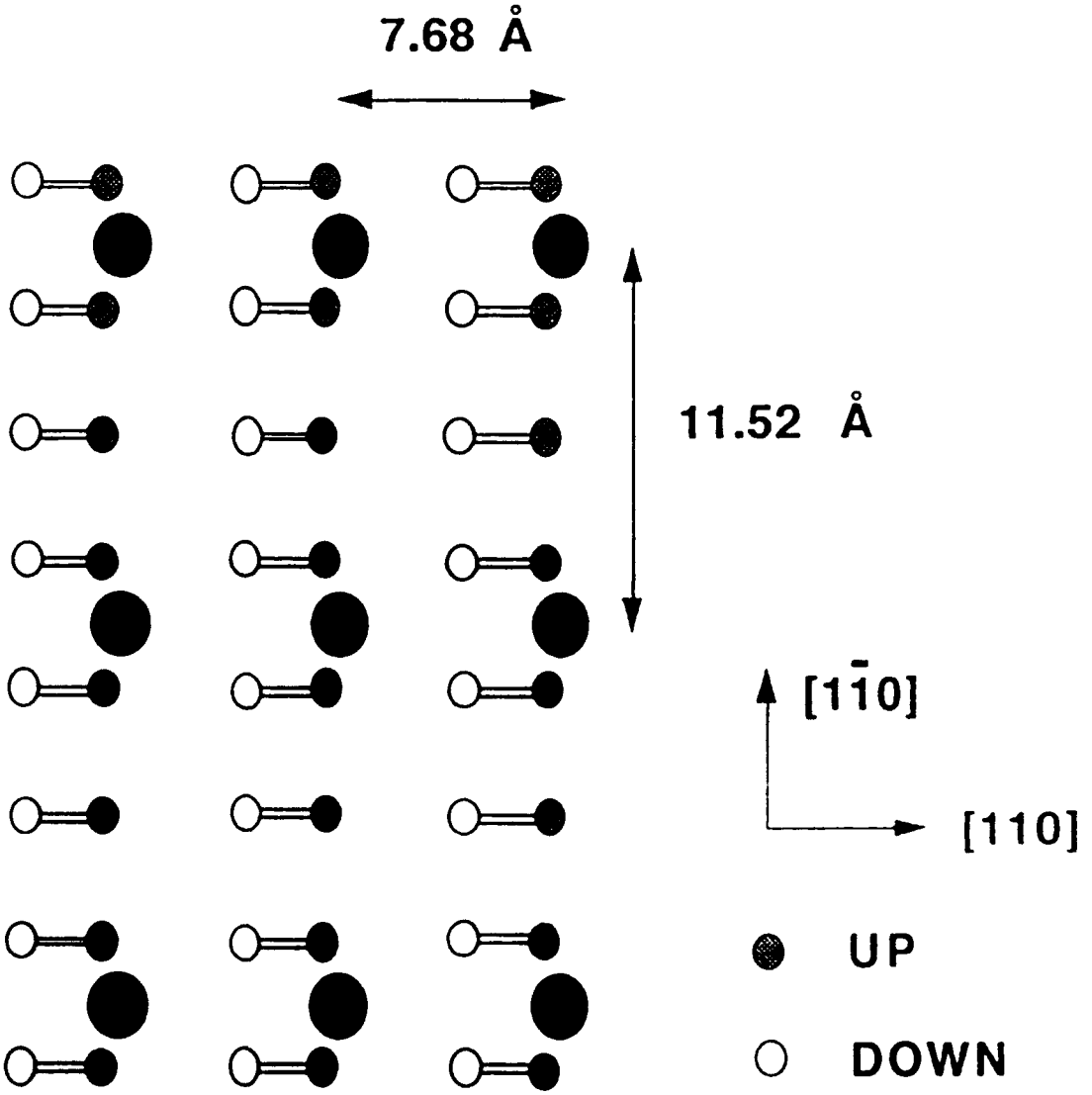

Fig. 2